Systematic variation of T_N(Pr) for the two-CuO_2-layer cuprate $m212$ ($m=1, 2, 3$) systems

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The systematic variation of anomalous Pr antiferromagnetic ordering temperature T_N(Pr) for the two-CuO_2-layer cuprate system $MA_2PrCu_2O_y$ (M=Cu, Hg, Tl, Pb; A=Ba, Sr) was verified through the observation of a new Hg-1212 $HgSr_2PrCu_2O_{6+\delta}$ tetragonal compound with a T_N(Pr) of 6 K and a Pr—O bond length of 2.492 Å between Pr and oxygen in the adjacent CuO_2 layers. For the tetragonal/orthorhombic 1212 compounds including the $PrBa_2Cu_3O_{7-y}$ system, T_N(Pr) was found to decrease monotonically with increasing Pr—O distance. The importance of Pr-O-Pr superexchange magnetic coupling is expected for all two-CuO_2-layer $M_mA_2PrCu_2O_y$ $m212$-type ($m=1$, 2, 3) compounds. A similar Pr anomaly in the 2212-type system was first observed on the new tetragonal $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$ compound with a high T_N(Pr) of 9 K. © *1996 American Institute of Physics.* [S0021-8979(96)02208-0]

The orthorhombic $PrBa_2Cu_3O_7$ compound with an anomalously high Pr antiferromagnetic ordering temperature T_N(Pr) of 17 K is the only nonsuperconducting member of the $RBa_2Cu_3O_7$ system (R=Y or a rare earth).[1–6] With further oxygen deficiency, T_N decreases to 10 K in tetragonal $PrBa_2Cu_3O_6$.[5,7] In comparison, other magnetic rare earth compounds have a maximum T_N(R) of 2.2 K in $GdBa_2Cu_3O_7$.[8,9] Since Pr is one of the lightest elements of rare-earth series, its $4f$ wave function is more extended and the anomalously high T_N observed indicates the importance of the quasi-two-dimensional (quasi-2D) Pr-O-Pr superexchange magnetic coupling through the strong hybridization between the Pr $4f$ and the eight O $2p_\pi$ orbitals in the adjacent two-CuO_2 layers.[6]

From the structural viewpoint, the 123-type $PrBa_2Cu_3O_{7-y}$ system can be recategorized as either the Cu-1212C-type (C stands for chain) for orthorhombic $[Cu]Ba_2PrCu_2O_7$ (space group $Pmmm$) or Cu-1212 $TlBa_2CaCu_2O_{7-\delta}$-type for tetragonal $[Cu]Ba_2PrCu_2O_6$ (space group $P4/mmm$),[10] analogous to other two-CuO_2-layer Pr compounds in the Tl-1212 $Tl(Ba,Sr)_2PrCu_2O_{7-\delta}$ system[11–15] and (Pb,Cu)-1212 $(Pb,Cu)Sr_2PrCu_2O_{7-\delta}$.[13] They also exhibit the common feature of having anomalous high T_N(Pr) values ranging from 4 to 8 K. The 12 K tetragonal $PrBa_2Cu_2NbO_8$ or $[Nb]Ba_2PrCu_2O_8$ compound can also be recategorized as the Nb-1212 $TlBa_2CaCu_2O_{7-\delta}$-type compound.[16]

Recently, a new Hg-1212 compound $HgSr_2PrCu_2O_{6+\delta}$ with the tetragonal $HgBa_2CaCu_2O_{6+\delta}$-type structure was reported where the mercury sample was prepared by two-stage solid-state reaction techniques where the precursor $Sr_2PrCu_2O_y$ powders were mixed with HgO powder, pressed into pellets, sealed in a 2 mm wall quartz tube in vacuum, and reacted at 1000 °C in vacuum for 8 h then quenched in liquid nitrogen.[17] A similar Pr anomaly is expected for this new compound. As shown in Fig. 1, a T_N(Pr) value of 6 K was identified from the minimum in the temperature derivative of the molar magnetic susceptibility $d\chi_m/dT$ in 1 T applied magnetic field. At higher temperatures, the temperature dependence of the magnetic susceptibilities indicates a magnetic Cu^{2+} ordering near 300 K or above. A simple Curie–Weiss fit $\chi_m=C^*/(T+\theta_p)$ below 200 K gives an antiferromagnetic-like, negative paramagnetic intercept $\theta_p=-13$ K and an effective magnetic moment of 3.31 μ_B per Pr from the Curie constant C^* if the small Cu^{2+} moment is neglected.[17] As in many other Pr cuprates, this effective moment is closer to that of the free Pr^{3+} ion (3.58 μ_B) rather than the Pr^{4+} ion (2.54 μ_B). Indeed, most experimental results on such compounds imply a Pr^{3+} state. The Pr magnetic transition of $HgSr_2PrCu_2O_{6+\delta}$ is clearly corroborated by low-temperature specific heat data $C(T)$ which show a distinct but broad magnetic transition prevails at T_N(Pr)=6 K and a very high onset around 11 K.[16] The broad transition indicates that a truly three-dimensional (3D) or quasi-2D long-range magnetic ordering set in at T_N(Pr)=6 K, while the 2D ordering effect persists up to the onset near 11 K.

The high T_N(Pr) observed in $HgSr_2PrCu_2O_{6+\delta}$ again indicates the importance of the quasi-2D Pr-O-Pr superexchange magnetic coupling through the strong hybridization between the Pr $4f$ and the eight O $2p_\pi$ orbitals in the adjacent CuO_2 layers. This degree of hybridization can be readily reflected in the Pr—O bond length, which can be accurately derived from the Rietveld analysis. X-ray Rietveld refinement on powder samples of tetragonal $HgSr_2PrCu_2O_{6+\delta}$ ($a=3.8532$ Å and $c=12.1199$ Å) gives a refined bond length d(Pr—O) between Pr and O(1) in the adjacent two-CuO_2 layers of 2.492 Å and the O(1)—Pr—O(1) bond angle is

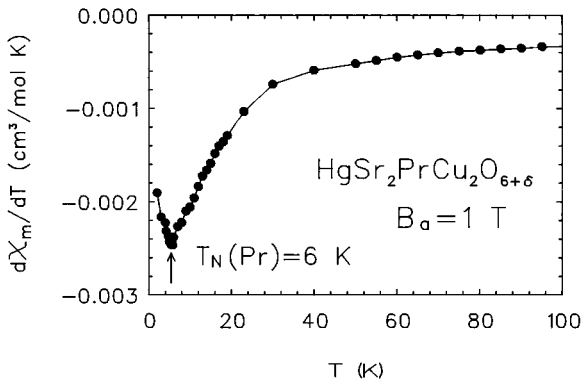

FIG. 1. Low-temperature differential molar magnetic susceptibility $d\chi_m/dT$ for a Hg-1212 $HgSr_2PrCu_2O_{6+\delta}$ compound revealing a T_N(Pr)=6 K.

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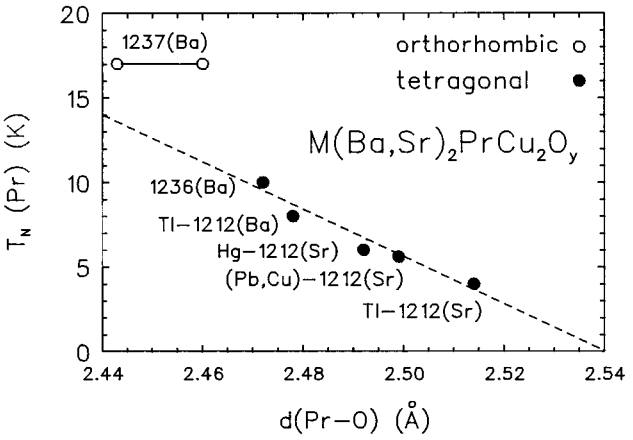

FIG. 2. T_N(Pr) vs Pr—O distance in various M(Ba,Sr)$_2$PrCu$_2$O$_y$ (M=Cu, Hg, Tl, Pb) 1212-type compounds. The dashed line is a guide to the eyes only.

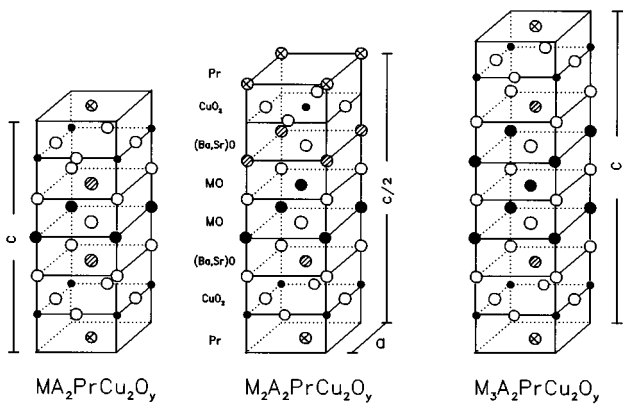

FIG. 3. Crystal structures of $M_mA_2PrCu_2O_y$ m212 (m=1, 2, 3; M=Cu, Hg, Tl, Pb; A=Ba, Sr) systems.

101.3°.[17] The d(Pr—O) for $HgSr_2PrCu_2O_{6+\delta}$, with T_N(Pr)=6 K, is shorter than 2.514 Å for Tl-1212(Sr) $TlSr_2PrCu_2O_{7-\delta}$ with T_N=4 K or 2.499 Å for (Pb,Cu)-1212 $(Pb_{0.6}Cu_{0.4})Sr_2PrCu_2O_{7-\delta}$ with T_N=5.6 K, but is longer than 2.478 Å for Tl-1212(Ba) $TlBa_2PrCu_2O_{7-\delta}$ with T_N=8 K.[13,14] This regularity forces us to study the systematic variation of T_N(Pr) for all reported M(Ba,Sr)$_2$PrCu$_2$O$_y$ (M=Cu, Hg, Tl, Pb) 1212-type compounds as a function of the Pr—O bond length as shown in Fig. 2. Note that for the orthorhombic T_N(Pr)=17 K 1237(Ba) $PrBa_2Cu_3O_7$ (Cu-1212C), instead of a single Pr—O bond length, there are two Pr—O bond lengths of 2.443 and 2.460 Å, respectively. For the oxygen-depleted tetragonal 1236(Ba) $PrBa_2Cu_3O_6$ (Cu-1212) compound, a single long Pr—O bond length of 2.472 Å with lower T_N(Pr) of 10 K was observed.[7] Clearly, T_N(Pr) decreases monotonically with increasing Pr—O bond length which reflects the degree of Pr $4f$–O $2p_\pi$ orbital hybridization or the strength of Pr-O-Pr superexchange coupling. Meanwhile, an effective coupling occurs between Cu and Pr moments through oxygen $2p_\pi/2p_\sigma$ as revealed by preliminary neutron and nuclear magnetic resonance studies on Tl-1212 Tl(Ba,Sr)$_2$PrCu$_2$O$_{7-\delta}$ system.[17] This competition should be taken into account before a final conclusion can be reached.

Various types of experiments have been performed to substantiate these anomalous Pr phenomena in the 123 or 1212 system to clarify the mechanism of magnetic order and/or superconductivity suppression, but a clear picture is still elusive. Obviously, additional information from more diverse systems would be extremely helpful toward delineating the various factors which may play crucial roles in this regard. Since in the high T_c cuprate systems, a total replacement of Ca by Pr between the CuO_2 layers can be achieved only in the tetragonal/orthorhombic two-CuO_2-layer $M_mA_2PrCu_2O_y$ m212-type structures (m=1, 2, 3; M=Cu, Hg, Tl, Pb and A=Ba, Sr), where the schematic structure comparison is shown in Fig. 3. Questions arise naturally whether the anomalous Pr effect occurs in 2212 $M_2A_2PrCu_2O_y$ or 3212 $M_3A_2PrCu_2O_y$ compounds. Only one 3212-type compound with a T_N(Pr) of 6–14 K was reported so far in the orthorhombic (Pb,Cu)-3212 $(Pb_2Cu)Ba_{2-x}Sr_xPrCu_2O_8$ system ($0\leqslant x\leqslant 1$), or commonly known as the 2213-type $Pb_2Ba_{2-x}Sr_xPrCu_3O_8$ system.[18] For the 2212-type compounds, no Pr ordering was observed down to 1.6 K for the orthorhombic Bi-2212 compound $Bi_2Sr_2PrCu_2O_8$.[19] However, via proper substitution, we are able to observe the first Pr anomaly in the tetragonal (Pb,Cu)-2212 $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$ compound (a =3.878 Å and c=27.594 Å). The sample was prepared by two-stage solid-state reaction techniques where the precursor $BaSrPrCu_3O_y$ powders were mixed with PbO powder and heated at 730 °C for 1 day and then pressed into pellets and sintered at 825–830 °C in flowing Ar for 3 days, then quenched in liquid nitrogen.[19] A fairly high T_N(Pr) value of 9 K was identified from the minimum in the temperature derivative of the molar magnetic susceptibility $d\chi_m/dT$ as shown in Fig. 4. In comparison, the isostructural compound $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2GdCu_2O_8$ exhibits a lower T_N(Gd) of only 2.2 K.[19] The magnetic transition can also be corroborated by low-temperature specific heat data $C(T)$ which show a distinct magnetic transition at T_N(Pr)=9 K with onset around 11 K.[19] The temperature dependence of the magnetic susceptibilities below 200 K indicates a simple Curie–Weiss fit $\chi_m=C^*/(T+\theta_p)$ which yields a negative paramagnetic

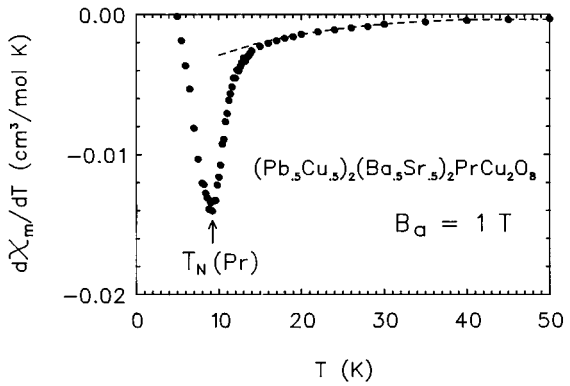

FIG. 4. Low-temperature differential molar magnetic susceptibility $d\chi_m/dT$ for (Pb,Cu)-2212 $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$ compound revealing a T_N(Pr)=9 K.

intercept $\theta_p = -10$ K and an effective magnetic moment of 3.22 μ_B per Pr.[19] The effective moment again is closer to that of the free Pr^{3+} ion. The magnetic entropy S_m associated with the Pr ordering has a lower limit, ~20% of $R \ln 3$ expected for Pr^{3+} with a quasi-triplet ground state. Accordingly, it seems reasonably to categorize the Pr ordering in this (Pb,Cu)-2212 compound as a three-dimensional-like ordering process. Confirmation requires detailed neutron diffraction studies.

The current results of anomalous Pr ordering on the new Hg-1212 compound $HgSr_2PrCu_2O_{6+\delta}$ and (Pb,Cu)-2212 compound $(Pb_{0.5}Cu_{0.5})_2(Ba_{0.5}Sr_{0.5})_2PrCu_2O_8$, along with earlier reports on other 1212- and 3212-type compounds, complete the demonstration of systematic of anomalous Pr ordering in all two-CuO_2-layer $M_mA_2PrCu_2O_y$ $m212$ ($m=1$, 2, 3) systems. Anomalously high T_N(Pr) observed for all compounds indicates the importance of the quasi-2D Pr-O-Pr superexchange magnetic coupling mechanism through the strong hybridization between the Pr $4f$ and the eight O $2p_\pi$ orbitals in the adjacent two-CuO_2 layers.

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